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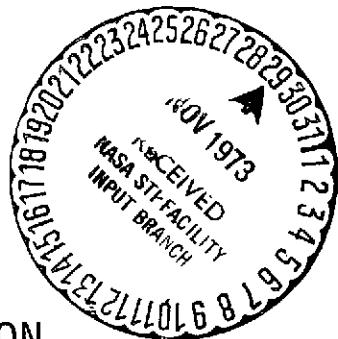
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**ANALYSIS OF MÖSSBAUER  $^{57}\text{Fe}$  ABSORPTION  
IN AN F. C. C. Fe-Co-V ALLOY**

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ABSTRACT

Mössbauer  $^{57}\text{Fe}$  absorption spectra of superparamagnetic F.C.C. Fe.34 Co.52 V.14 (Vicalloy II) have been analysed using a cluster model and magnetic resonance relaxation theory. The number and magnetic moment of the clusters were determined from magnetization data. A least-squares fit to the spectrum at 4.2 K gives  $H_{\text{hyp}} = 175$ . kG, substantially greater than the value 55 kG inferred just from the observed broadening of the single-line spectrum. From this broadening an estimate of 40 kG is obtained for the width of the distribution in  $H_{\text{hyp}}$  at 4.2 K arising from compositional fluctuations and small-cluster effects. The model can be applied to unresolved or poorly resolved Mössbauer spectra in conjunction with superparamagnetic magnetization data in multi-component single-phase alloys of arbitrary composition.

I. INTRODUCTION

In the investigation of weakly magnetic systems using the Mössbauer effect, unresolved or poorly resolved spectra are frequently encountered, which can persist over a wide temperature range.<sup>1-6</sup> The coexistence of several non-instrumental broadening mechanisms can make the interpretation of such spectra difficult. In particular Wickman has shown how magnetic resonance relaxation theory can be applied in the analysis of Mössbauer paramagnetic hyperfine structure arising from spin relaxation effects.<sup>2</sup> Lundquist et al have applied this theory to superparamagnetic Ni particles, using a simplified model for the spin relaxation.<sup>3</sup> In this paper we apply the theory to F.C.C. Fe.34 Co.52-V.14 (Vicalloy II). Allowance is made for the possibility of more than one superparamagnetic cluster size and corresponding cluster relaxation time. Although the effect of compositional fluctuations are not included explicitly in the model, an estimate of the width of the distribution of hyperfine fields is obtained from a consideration of the residual broadening at low temperatures.

II. CLUSTER MODEL FOR F.C.C. VICALLOY

We wish to describe a disordered, single-phase superparamagnetic alloy in terms of a cluster model. Such models have been used in discussing the magnetization of many superparamagnetic binary alloys.<sup>7</sup> Thus at a given temperature  $T$ , we assume that the alloy consists of superparamagnetic regions separated by paramagnetic regions. This fine-grained magnetic inhomogeneity is presumed to arise from compositional fluctuations. We assume that each super-paramagnetic "cluster" has a magnetic ordering temperature  $\theta$ , with  $T < \theta$ , which results in a non-vanishing net moment  $\vec{\mu}$ , the direction of which changes in a random

manner with a characteristic spin-flip time  $\tau$ . This quantity depends on the cluster volume  $\Omega$  through the bulk anisotropy energy  $E_a$ ; for zero applied field we have

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (1)$$

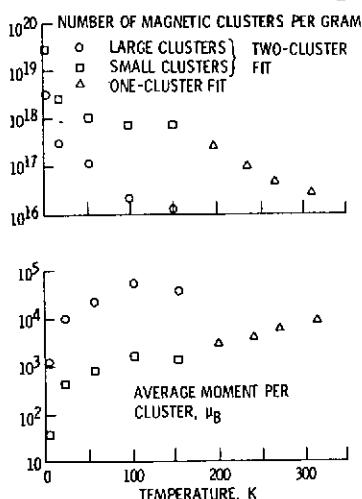
where the pre-exponential factor  $\tau_0$  is, for  $T \ll 0$ , of the order of the inverse of the Larmor precession frequency  $\omega_L(H_C) = \gamma H_C$  of the electronic spin in the anisotropy field  $H_C$ .<sup>8,9</sup> If we assume that the first-order anisotropy constant  $K_1$  gives the major contribution to  $E_a$  and that the [111] direction is the easy direction in F.C.C. Vicalloy, then  $E_a = |K_1| \Omega / 12$ . The Larmor frequency for this case ( $K_1 < 0$ ) is given by  $4\gamma |K_1| / 3(\mu/\Omega)$ ,<sup>10</sup> so we take

$$\tau_0 = 3/4 \frac{\mu}{\gamma |K_1| \Omega} \quad (2)$$

In general we expect there to be a distribution of cluster sizes. The exchange interaction between clusters, although weak, will be sufficient to cause existing clusters to coalesce and new ones to form, as the temperature is lowered. Hence the distribution will be rather sensitive to temperature. Previous work on F.C.C. Vicalloy II indicates that this alloy is superparamagnetic down to 4.2 K.<sup>1</sup> The Mössbauer data show a slightly broadened single-line spectrum at 300 K which broadens with decreasing temperature without development of resolvable hyperfine splitting. The magnetization data was analysed in Ref. 1 assuming only one size of cluster at given  $T$ , and indicated the presence of a large number of small clusters at low  $T$ . The data has therefore been reanalyzed for  $T \leq 150$  K assuming two different cluster sizes at each  $T$ , one "large" and one "small". If we treat the clusters as non-interacting, then the sample magnetization is

$$M(H, T) = \mu_L N_L L\left(\frac{\mu_L H}{k_B T}\right) + \mu_s N_s L\left(\frac{\mu_s H}{k_B T}\right) + \chi_p(T) \cdot H, \quad (3)$$

for  $T \leq 150$  K, where  $N_{L,S}$  and  $\mu_{L,S}$  are the number per unit volume and moment of the large and small clusters, respectively, and  $\chi_p(T)$



is the susceptibility of the paramagnetic regions. This results in a substantially better fit to the data, and the variation of the cluster parameters with  $T$  is shown in Fig. 1. The points for  $T > 150$  K were obtained previously using the single-cluster fit. As in Ref. 1, the parameters of Fig. 1 can be used to obtain an average moment  $\langle \mu_a \rangle$  per magnetic atom, shown in Fig. 2.

The Mössbauer  $^{57}\text{Fe}$  Absorption spectrum  $I(\omega)$  at a given temperature for zero applied field can be similarly written as

$$I(\omega) = C \left[ f_L I_o(\tau_L, \omega) + f_s I_o(\tau_s, \omega) + f_p I_o(\tau_p, \omega) \right], \quad (4)$$

Figure 1. - Cluster parameters vs. temperature for F.C.C. Vicalloy II, determined from magnetization data of Ref. 1 using a two-cluster fit for  $T \leq 150$  K.

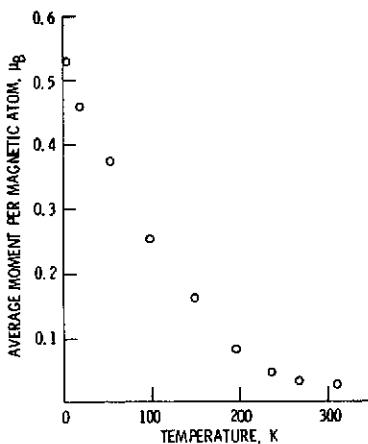


Figure 2. - Average moment per magnetic atom vs. temperature obtained from the parameters of fig 1.

hyperfine field. The cluster volumes are not directly determinable from the data. At sufficiently low  $T$  their values can be inferred by assuming that the clusters have a common magnetization and that the decrease in  $\langle \mu_a \rangle$  with  $T$  in Fig. 2 is brought about by an identical decrease in  $(f_L + f_S)$  from a value of unity at  $T = 0$ . Thus taking

$$f_L(T) + f_S(T) = \langle \mu_a(T) \rangle / \langle \mu_a(0) \rangle , \quad (5)$$

$$\frac{\mu_L}{\mu_s} = \frac{\mu_s}{\mu_s} , \quad (6)$$

enables us to obtain  $\Omega_L$  and  $\Omega_S$  and hence  $f_L$ ,  $f_S$  and  $f_p$ . From Eq. (6), the value of  $\tau_0$  is the same for the two cluster sizes. The paramagnetic relaxation time  $\tau_p$  is taken to be  $\tau_0$ . The quantity  $|K_1|$  is not known, but together with  $H_{hyp}$  gives a set of two parameters which can be fitted to the spectrum at low  $T$  using Eq. (4). To obtain a good fit in the neighborhood of the absorption maximum, it was found necessary to convolute the data with a Gaussian broadening function of full width  $2\delta$ . The results of a least-squares fit at 4.2 K with  $|K_1|$ ,  $H_{hyp}$  and  $\delta$  as parameters is shown in Fig. 3.

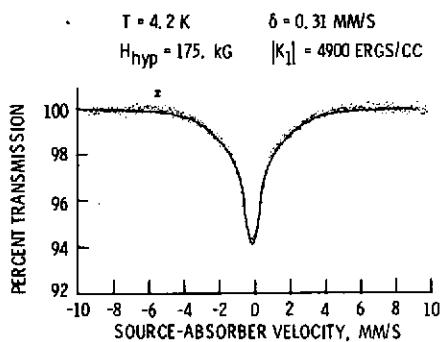


Figure 3. - Mössbauer  $^{57}\text{Fe}$  spectrum at 4.2 K. The calculated curve is a least-squares fit using a relaxation model with the parameters indicated.

In order to take into account the effects of finite  $\theta$  at higher  $T$  we do not use Eq. (5) but assume  $H_{hyp} \propto \mu/\Omega \propto \tau_0$ , while retaining Eq. (6). The proportionality constants were determined from the results at 4.2 K. For the value of  $K_1$  appearing in the exponent in Eq. (1) we use the value determined at 4.2 K. The error introduced is small since it turns out that the Boltzmann factor is nearly unity at all temperatures investigated.

where  $f_L = \Omega_L N_L$ ,  $f_S = \Omega_S N_S$  and  $f_p = 1 - (f_L + f_S)$  are the fractions of the sample consisting of large clusters, small clusters and paramagnetic regions, respectively. The parameter  $C$  fixes the scale of the absorption at each  $T$  and was determined from the experimental data by fitting the integrated area under  $I(\omega)$  to the observed total sample absorption. The expression for  $I_o(t, \omega)$  has been derived by others using magnetic resonance relaxation theory based upon the modified Bloch equations.<sup>2,11</sup> It depends implicitly on the hyperfine field  $H_{hyp}$  and the isomer shift  $v_0$ . In this paper no attempt was made to analyze the magnitude of  $v_0$  or its variation with  $T$ . The unknown parameters entering Eq. (4) are therefore the cluster volumes, the relaxation times and the hyperfine field. The cluster volumes are not directly determinable from the data. At sufficiently low  $T$  their values can be inferred by assuming that the clusters have a common magnetization and that the decrease in  $\langle \mu_a \rangle$  with  $T$  in Fig. 2 is brought about by an identical decrease in  $(f_L + f_S)$  from a value of unity at  $T = 0$ . Thus taking

$$f_L(T) + f_S(T) = \langle \mu_a(T) \rangle / \langle \mu_a(0) \rangle , \quad (5)$$

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### III. RESULTS AND CONCLUSIONS

The parameters resulting from a least-squares fit to the spectra at various T are shown in Table I. Included is an estimate of the cluster diameter D obtained assuming spherical clusters. The values of N and  $\mu$  for the clusters were determined for each T by linear interpolation between the data of Fig. 1. The value of  $|K_1|$  is  $4.9 \cdot 10^3$  ergs/cc, indicating a weak magnetic anisotropy. In fact the exponent

Table I. Values of H,  $\tau_o$ ,  $f_p$ ,  $2\delta$  and D obtained from a least-squares fit to the data

T (K)	$H_{hyp}$ (kG)	$\tau_o (10^{-8} s)$	$f_p$	$2\delta$ (mm/s)	$D_L$ (A)	$D_S$ (A)
4.2	175.	.30	.032	.62	38.	12.
25.	151.	.26	.056	.46	84.	30.
75.	111.	.19	.131	.18	134.	43.
150.	69.	.12	.246	.22	162.	52.
300.	55.	.10	.832	.20		105.

in Eq. (1) is so small that  $\tau$  never exceeds  $\tau_o$  by more than five percent. Therefore, for this system at least, it appears that including more than one cluster size makes very little difference in the analysis of the Mössbauer data. On the other hand the variation of  $H_{hyp}$  with T should resemble a Brillouin function if the clusters are characterized by a unique Curie temperature  $\Theta$ . The plot of  $H_{hyp}$  versus T given in Fig. 4 shows that this is not the case. We therefore regard our  $H_{hyp}$  as some average over a distribution of hyperfine fields.

Such a distribution can arise for small clusters from variations in composition (and hence in  $\Theta$ ) from cluster to cluster and also from the dependence of  $\Theta$  on cluster volume (and cluster shape). The critical cluster diameter for the onset of these size effects is of order 100 Å or less, which is the case here. (If the cluster size turned out to be greater than a few hundred Ångströms our model would actually be inconsistent, since multiple-domain formation would occur.) These small-cluster effects have been neglected in our model. Eq. (6), for example, essentially assumes that  $\Theta$  is independent of cluster size. However an estimate of the width of the distribution of  $H_{hyp}$  at low T can be obtained in the following way. We assume that the constancy of  $2\delta$  at  $\sim 20$  mm/s

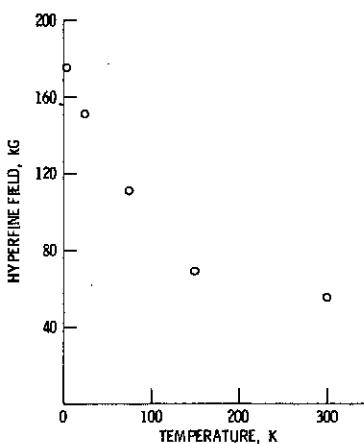


Figure 4. - Hyperfine field vs. temperature.

for  $T \geq 75$  K represents an essentially temperature-independent collision-induced broadening arising from the finite sample thickness; such a broadening corresponds to about three detector channel widths and seems to us to be a reasonable estimate of the instrumental broadening. The additional broadening at 25 K and 4.2 K we attribute to a distribution of  $H_{hyp}$ . Eq. (4) can then be used to determine the increase in  $H_{hyp}$  required to make up the difference. The result is about 20 kG. This can be interpreted as the half-width of a distribution having a mean value of 175 kG. Thus  $H_{hyp} = (175. \pm 20.)$  kG, which is substantially larger than the value of 55 kG inferred just from the observed line broadening.

The distribution in  $H_{hyp}$  presumably exists at higher T, but the fall-off with T of the mean  $H_{hyp}$  and the corresponding relaxation time combine to give an intrinsically narrower Mössbauer line, and this is why we do not consider the effect of the distribution of  $H_{hyp}$  on the observed line width at higher T.

Linear extrapolation of Fig. 2 to zero average moment gives 510 K as the point where superparamagnetic behavior disappears. Fig. 4 indicates that there are relatively few clusters large enough really to have a Curie point this high.

The magnetic coupling of the iron in the clusters is not known, but may be ferrimagnetic or antiferromagnetic. It is known that metallic Fe in an F.C.C. matrix tends to be antiferromagnetic. Furthermore the small average moment of the system is difficult to account for if all the magnetic atoms couple ferromagnetically, but can be explained rather simply if it is assumed that the Fe makes no net contribution to the moment while that contributed by the Co is reduced by the V by an amount roughly equal to that in an F.C.C. Co-V alloy having the same V/Co atom ratio.

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